ESTCP
Cost and Performance Report

(CP-9805)

Removal, Separation, and Recovery of Heavy Metals from Industrial Wastestreams Using Molecular Recognition Technology (MRT)

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COST & PERFORMANCE REPORT
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LIST OF ACRONYMS

ATMA	Automated Trace Metal Analyzer
Cr (VI)	Hexavalent Chromium Ion
Cr (III)	Reduced Chromium Ion
CWA	Clean Water Act
DoD	Department of Defense
EDTA	Ethylenediaminetetraacetic Acid
ESTCP	Environmental Security Technology Certification Program
F006	Designation of Hazardous Waste Under 40 CFR 261.31
gpm	Gallons Per Minute
ICP	Inductively Coupled Plasma
IWPF	Industrial Wastewater Pretreatment Facility (term used for this report)
IWTP	Industrial Wastewater Treatment Plant (generic term)
LM2+	Ligand-Metal Complex for metals Ag^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}
M2+	Alkaline Earth Metals (Mg^{2+}, Ca^{2+})
M+	Alkali Metals (Na^{+}, K^{+})
MP&M	Metal Products and Machinery (Rule)
MRT	Molecular Recognition Technology
NFESC	Naval Facilities Engineering Service Center
NSPS	New Source and Performance Standards
O&M	Operations and Maintenance
POTW	Public Owned Treatment Works
ppm	Parts Per Million
PSNS	Puget Sound Naval Shipyard
PSES	Pretreatment Standard for Existing Systems
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
USEPA	U.S. Environmental Protection Agency
WDOE	Washington Department of Ecology

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1.0 EXECUTIVE SUMMARY

All Navy, Army, and Air Force industrial wastewater treatment plants (IWTPs) receive 90% by volume of metal laden wastewaters from electroplating, parts cleaning and paint stripping operations. Treatment of industrial wastewaters using the conventional hydroxide precipitation method generates hazardous metal sludge, which is sent to landfill as RCRA F006 hazardous waste. With increasing potential for "out of compliance violations" (ref. 1) under the Metal Products and Machinery (MP&M) Rule-40 CFR Part 438, Naval Facilities Engineering Service Center (NFESC) was tasked by the Office of Naval Research (ONR) to develop and demonstrate innovative industrial wastewater treatment technologies. This effort was part of a Tri-Service program to evaluate advanced techniques to effectively recycle/reclaim metals from industrial wastewaters (ref. 2).

An industrial process was sought that would selectively recover heavy metal ions and not retain the benign alkaline earth metal ions such as Na+ and K+ or alkali metal ions Mg2+ or Ca2+. In 1995, a NFESC published the results of feasibility testing of three novel metal adsorption technologies (ref. 3). One of these metal adsorption technologies, for which IBC Advanced Technologies, Inc., holds patents, met the Navy's treatment requirements for heavy metal recovery/recycle from acid/alkali cleaning process wastewaters and chromium plating rinse waters. This metal recovery process is based on the use of synthetic chemical compounds called macrocyclic ligands, a concept that received the 1987 Nobel Prize in chemistry (ref. 4). These highly selective macrocyclic ligands will complex with heavy metals ions and have very weak interactions with benign alkaline earth or alkali metal ions. The term, "molecular recognition" has been applied to macrocyclic ligands that are capable of single metal ion selection. These highly selective macrocyclic ligands are attached to solid supports such as silica or polyacrylate and the resulting commercial product has been trademarked as Superlig®. Molecular recognition technology (MRT) applications are numerous, from metal recovery and removal of impurities to effluent polishing.

The objective of this project was to demonstrate the technical performance and life cycle cost of MRT at Puget Sound Naval Shipyard (PSNS). This alternative metal recovery/recycle process was evaluated on its capability to: (1) ensure DoD's metal finishing facilities can remain in compliance with federal, state and local regulatory discharge limits, and (2) significantly increase pollution prevention opportunities for elimination of hazardous sludge and recycling metal laden hazardous waste to recycle/reclaim vendors.

Wastewater discharges into surface waters are governed under the Clean Water Act, which established the National Pollutant Discharge Elimination System (NPDES). Industrial wastewater discharges from DoD IWTPs have specific discharge limits dependent on whether the industrial operation discharges directly to a waterway or indirectly through a sewage treatment facility or publicly owned treatment works (POTW).

The results of the demonstration, which was conducted at PSNS from 1999 to 2001, showed that MRT successfully recovered all heavy metals regulated under the CWA pretreatment standards. The metal ion concentration in the effluent stream was two orders of magnitude below PSNS monthly regulatory discharge limits and much lower than with the conventional precipitation technology. The analytical results showed that benign alkaline earth and alkali metals passed through the MRT column as predicted. Due

to the passage of these benign metals, the mass balance analysis confirmed the MRT column capacity was five orders of magnitude greater than typical ion exchange columns.

In order to obtain the recycle capability of MRT, which would reduce infrastructure at DoD facilities, MRT has a small footprint and ancillary equipment is minimal, ion exchange would require additional equipment such as electrowinning or electrodialysis (ref. 5).

The cost savings and payback for a complete MRT industrial wastewater treatment facility are largely dependent on future liability costs of land filling RCRA F006 sludge. Revenues from metal recycle companies are lacking at DoD facilities due to existing DoD facility/regional-wide hazardous landfill disposal contracts. For the purposes of this report, RCRA F006 disposal costs were average over of 14 DoD IWTPs as $67,000 per year (ref. 6).

Six different cost estimates were made for MRT due to the versatility of the technology. The longest payback period was for an MRT installed as a replacement system at PSNS. The ECAM showed a payback of 9 years. The cost savings of MRT over the conventional system (base process system) was estimated to be $73K per year. If MRT were used as an add-on for pretreatment of chelated copper, the payback would be 2.5 years. For a polishing system MRT system using embedded membranes, the payback could be <1 year.

Previous efforts by DoD have been to reduce the volume of IWTP sludge, and not to eliminate sludge going to landfill by either recycling to process or making the sludge amenable for selling the metal recycle vendors. The MRT system of metal recovery/recycle provides an alternative to the conventional precipitation treatment in DoD's IWTPs. Secondly, MRT can be selective for only the regulated metals produced by the activity's industrial operations.

2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

Heavy metal ions are among the most common toxic components in wastewaters from DoD industrial operations. At PSNS, the industrial wastewater pretreatment facility (IWPF) can receive large volumes (> 1 million gallons/year) of metal laden wastewaters. At PSNS, the metal finishing facility generates 90% of the volume distributed as (1) 56 % acid/alkali cleaning wastewaters, (2) 35 % chromium plating rinse waters, and (3) 9 % cyanide process wastewaters. Hydroxide precipitation is the conventional method for removal of heavy metals from these three influent waste streams. This treatment process generates hazardous sludge, classified as F006 hazardous waste under RCRA, and currently sent to a landfill.

In order to avoid generation of metal contaminated F006 sludge, an alternative technology must be capable of recovering heavy metals such that they are selectively or sequentially segregated from the industrial waste stream. An additional requirement that must be met is that this technology be amenable to recycle the product to process or resale to metals recycle vendor. In DoD facilities, the removal of heavy metals below discharge standards will be in the presence of other dissolved solids. Besides heavy metal contamination, industrial wastewaters contain large concentrations of alkali metals such (Na+, K+) and alkaline earth metals (Mg2+, Ca2+), which are not regulated and need not be removed from the wastewater. Although ion exchange offers good binding toward heavy metals, the technology is not selective to that class of metals alone. Alkali/alkaline earth metals, as well as heavy metals, may bind to ion exchange resin and reduce efficiency by rapidly loading the binding sites and increasing the number of regeneration cycles.

A major research interest over the last three decades has been investigation of an alternative chemical sorption/desorption process that would only selectively bind heavy metals desired to be recovered. The approach has been called molecular recognition technology (MRT). Molecular recognition uses one chemical structure called the host, to recognize specific electronic and spatial features of another chemical called the guest, to form a "host-guest" complex. A guest, such as a dissolved ionic metal species, can be selectively removed from solution by being complexed with host chemical and thus be isolated for later recovery. Ligand is a term defined as any molecule or ion that has at least one electron pair that acts as a donor atom (i.e., S, N, O). Figure 1 shows oxygen and nitrogen electron pair donors in

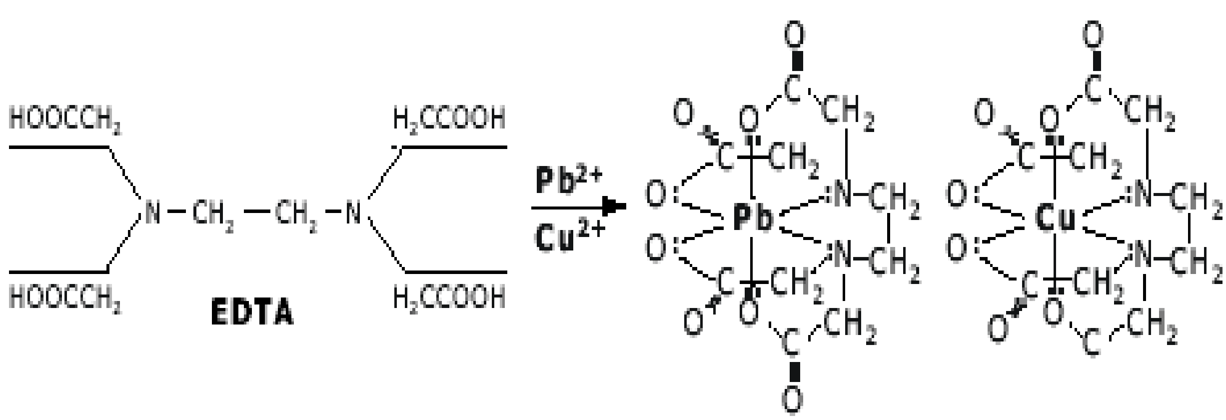

Figure 1. EDTA Non-Specific Selectivity for Copper and Lead.

ethylenediaminetetraacetic (EDTA). As shown in Figure 1, the selectivity for a specific contaminant metal does not occur with EDTA and both copper and lead are equally chelated (ref. 4,7).

In Figure 2(a), copper is selectively removed over lead n the waste stream by the Superlig®. Chemically, the macrocyclic ligand adsorption process is based on two factors, 1) metal iondipole interaction between the heavy metal and the negatively charged donor atoms placed in the macrocyclic ligand and 2) the size and geometry of the macrocyclic cavity. This ion-dipole interaction between the heavy metal cation and negatively charge donor atoms (O, N, S) is shown in Figure 2(a) Figure 2(b) shows examples of a wide range of patented macrocyclic polyether ligands attached to solid supports that can sequester metal cations (ref. 3,7). The capability to form complexes with heavy metals can be calculated from each ligand's deprotonation and ligand-metal stability constants (log K) (ref.. 7,8). Table 1 gives metalbinding stability constants (K) for one particular Superlig® and for comparison, various chelating and ion exchange resins. Chelating or typical ion exchange resins normally have binding constants of 1010 or 103, respectively. MRT has binding constants as high as 1050.

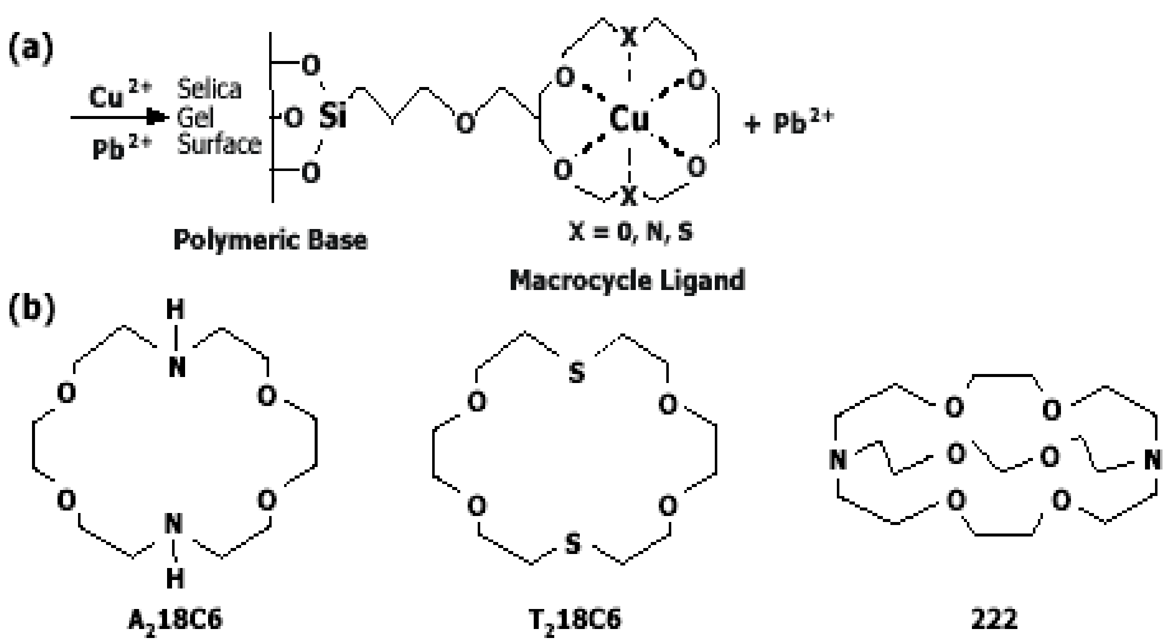

Figure 2. (a) Metal Ion Selectivity for Specific Metal Recovery, and (b) Patented Macrocyclic Ligands.

Table 1. Metal-Binding Stability Constants (Log K) for Superlig®, Cation Ion Exchange and Chelating Ion Exchange.

Cation	Superlig®	Regular IX Active Sulfonic Acid Group	Chelating IX Active Iminodiacetic Acid Group
Mg^{2+}	0.02		
Cd^{2+}	13.8	<0.7	3.0
Cr^{3+}	30.0	<0.7	
Cu^{2+}	22.0	<0.7	7.3
Ni^{2+}	17.0	<0.7	4.9
Pb^{2+}	14.4	<0.7	4.2
Zn^{2+}	14.4	<0.7	3.8
Ag^{2+}	13.8	<0.7	<0.7

2.2 PROCESS DESCRIPTION

The Superlig® materials may be embedded in membranes, replaceable cartridges or as the more tradition packed bed column configuration as demonstrated at PSNS (ref. 9). Depending on metals to be removed from the waste stream, the selected Superlig® is placed in a packed bed column configuration as shown in Figure 3. The graphic shows the process steps for selective removal of copper. The waste stream is passed through the column and copper is adsorbed on the MRT column. The column is then regenerated to obtain a highly purified copper metal concentrate that is drummed. This drummed concentrate my be recycled to process or sold to an appropriate metal recycle vendor as described in section 6.1.2. Other metals Cr (III), Ni, and Cd pass through the column as shown in Figure 3.

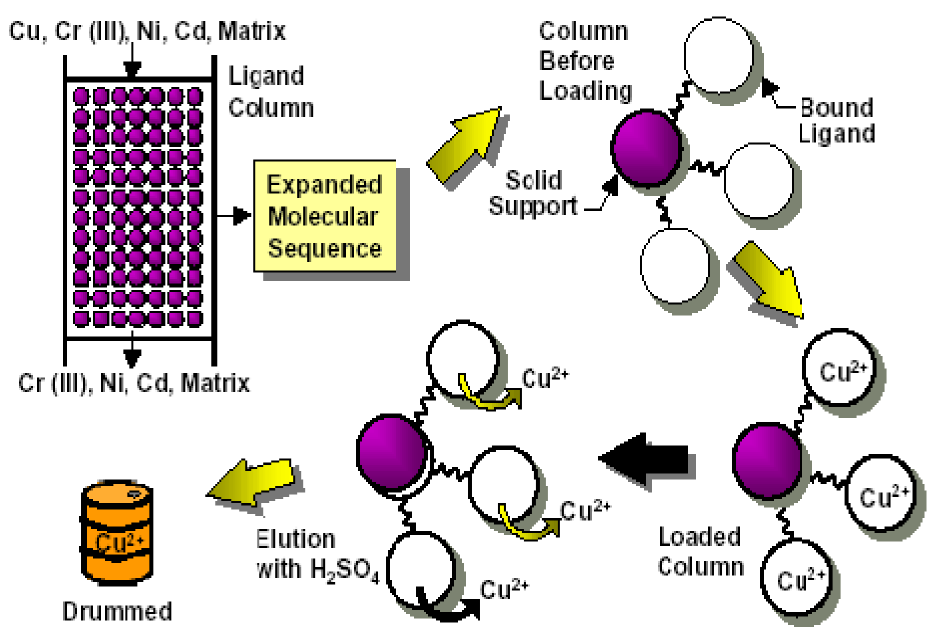

Figure 3. MRT Column for Cu2+ Recovery Showing Final Product Concentrate for Recycle.

At PSNS, MRT was demonstrated for acid/alkali waste stream with a mixed packed bed column to capture all regulated heavy metals, Cu, Cd, Cr (VI, III), Ni, Pb, Zn, and Ag. Table 2 shows the processing steps. The columns are conditioned in step 1 & 2. In step 3, the feed solution is run through lead-trail columns containing the appropriate Superlig® to remove the targeted metal ion(s). The metal ion(s) are captured and held by the Superlig® while the bulk solution passes through the column. After the lead column is saturated with the target metal ion(s), the feed is diverted. The captured metal ion(s) are eluted (or stripped) from the column with 4 M sulfuric acid (or other appropriate solution) as shown in step 5. The eluate contains an acidic, concentrated, pure metal ion sulfate stream. After regeneration with NaOH in step 1, the column is ready to receive wastewater feed once again. Table 2 shows final destination of process wastewaters. For the demonstration of Cr (VI), the same steps were followed on Table 2 as for the acid/alkali waste stream.

Table 2. Description of MRT Cycle Processing of Wastewaters.

Step	Input Stream	Column Action	Output Stream	Final Destination
1	Dilute NaOH	Neutralizing Protonated Bound Ligand	Dilute Na_2SO_4	Sewer
2	H_2O	Wash Out Na_2SO_4	H_2O/Na_2SO_4	Sewer
3	Acid/Alkali Feed	Removal of Heavy Metal(s)	Feed Effluent Metals	Sewer
4	H_2O	Wash Through Remaining Feed	Feed Effluent Metals	Sewer
5	Dilute H_2SO_4 Elution	Strip Heavy Metal(s)	Small Volume Heavy Metal(s) SO_4^{2-} Concentrate	Collection as Product for Recycle Process or Sell Metals Recycler

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

2.3.1 MRT Advantages

Future industrial wastewater treatment facilities will require closed loop systems that discharge little or no pollutants to the environment. MRT has a number of advantages for this application as summarized below.

1. The highly selective ligands give MRT the ability to remove selected metals to extremely low levels, often several orders of magnitude below current discharge limits. These lower limits do not require pH adjustment.

2. The design features of MRT allow creation of ligands selective for only the ion of interest in the presence of high concentrations of competing ions.

3. The ability to design selective ligands with targeted stability constants allows a range of elution options. Eluents can be chosen that are compatible with industrial wastewater chemistry and therefore recycle of the eluent will be a possible option.

4. Rapid kinetics are possible, which allows high flow rates. For very low influent metal levels, affinity membranes can be used for even higher flow rates and rapid processing.

5. MRT can be fully automated for continuous operation and has small space requirements.

6. If chelating agents are present in an industrial waste stream, pretreatment prior to bulk precipitation by NaOH must be conducted. The PSNS MRT demonstration showed that pretreatment for surfactants and chelating agents was not required for recovery/recycle of metals. Feasibility studies at NAS North Island showed that the MRT processing broke the chemical bond between the chelating agent and copper.

7. MRT can be used as a polishing system for specific metals out of compliance at an IWPF.

8. Due to the simplicity of the process, and highly efficient elution curves, there is a reduction in the volume of process chemical required for MRT.

9. MRT technology can enable DoD facilities to meet the MP&M proposed future discharge limits for tin, molybdenum, and manganese.

2.3.2 MRT Limitations

The limitations of this technology are more based on site specific factors than the general technology. The following concerns should be evaluated before procuring an MRT system.

1. There are several different MRT systems that can be configured to meet the requirements of a DoD facility. At PSNS, feasibility tests with both column and membrane configurations were conducted. The packed bed column configuration showed better results for batch operation of high volumes and metal concentrations greater than 50ppm.

2. If the particulate matter in the wastewater is greater than 15 microns, then it is advised to use a pretreatment filtration system.

3. The technical level of the operators requires training beyond the standard wastewater treatment operator certificate.

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3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

The objective of this project was to demonstrate the adsorptive metal recycle/reclaim capability of MRT. MRT must meet and exceed the current federal discharge standards under the CWA, as well as local discharge limits to POTWs. These limits were the first primary criteria. MRT must be more cost effective over other adsorptive metal recovery technologies, which were the second primary performance criteria. MRT must also demonstrate metal ion selectivity by showing a 98% extraction of the specific metals from the industrial waste stream. A pollution prevention credit will be gained in reducing or eliminating the metal hydroxide sludges.

Table 3. Performance Objectives.

Performance Objective	Primary Performance Criteria	Expected Performance	Actual Performance
Quantitative	1. Exceed CWA Limits	½ Discharge Limit	Met ½ Discharge Limit
	2. Capital Cost Less Conventional	Lower	45K (%) higher
	3. Extraction of Specific Metals	98%	98.9%
	4. Efficiency > Related Technology	80%	60%
	5. Sludge	95%	90%
Qualitative	6. Ease of Use	Minimal Training	Training 1 Yr>IWTP Operator

3.2 SELECTION OF TEST SITE FACILITY

Puget Sound Naval Shipyard (PSNS) was selected because it is typical of other DoD maintenance and repair facilities. Since 1998, PSNS has been researching the future requirements for an industrial wastewater treatment plant. The ESTCP demonstration/validation project was proposed for PSNS because they were evaluating alternative wastewater treatment technologies that would increase the capability of moving toward a “zero discharge” for a new industrial wastewater pretreatment facility.

3.3 TEST FACILITY HISTORY/CHARACTERISTICS

PSNS is engaged in extensive maintenance work on small and large Naval vessels. Work is heavy industrial, including metal plating and cleaning operations such as etching, passivating, plating, galvanizing, and general cleaning. Over 90% of the wastewaters to the IWPF come from the Metal Preparation Facility. The IWPF receives waste by tank delivery in minimal quantities from the sheet metal shop and the photo laboratory. These processes generate rinse water that must be pretreated before discharge to the local sanitary facility or POTW. In 1976, PSNS constructed an Industrial Wastewater Pretreatment Facility to treat industrial wastes from several industrial shops throughout the shipyard. All process equipment is located within the building, and the only external activity is unloading of wastewater from portable tanks and process chemicals, and loading of sludge to be hauled to the Hazardous Waste Containing Storage Area.

There are three waste steams that constitute the major volume of influent to the PSNS IWPF: 1) chromium electroplating; 2) cyanide rinse and dip; and 3) acid/alkali from cleaning operations. The cyanide waste stream is pretreated for destruction of the free cyanide by oxidation with sodium hyprochlorite (NAOCl), and chromium (VI) is reduced with ferrous sulfate to chromium (III). After a neutralization step, the three latter waste steams become a single, integrated waste stream where the metals are precipitated as metal hydroxides using caustic soda (NaOH). See Figure 4 for treatment processing steps. This metal hydroxide sludge is de-watered, transported to the Treatment, Storage, and Disposal Facility (TSDF), and then disposed of in a RCRA Subtitle D landfill. The treated wastewater, after analytical testing, is released to local sanitary sewer plant. The PSNS IWPF operates under RCRA "permit by rule" exempting it from requiring a Part B Permit under the regulations of the Clean Water Act. The gray shaded rows in Table 4 indicate MP&M proposed changes to the discharge limits for additional metals of tin, molybdenum, manganese. In procuring future IWPF treatment processing, the PSNS must consider future workloads. The proposed MP&M effluent standards are for treatment plants with greater than 1 million gallons per year. PSNS volumes for effluent discharge are less than 1 million gallons per year, but may change as the workload in the shipyard changes.

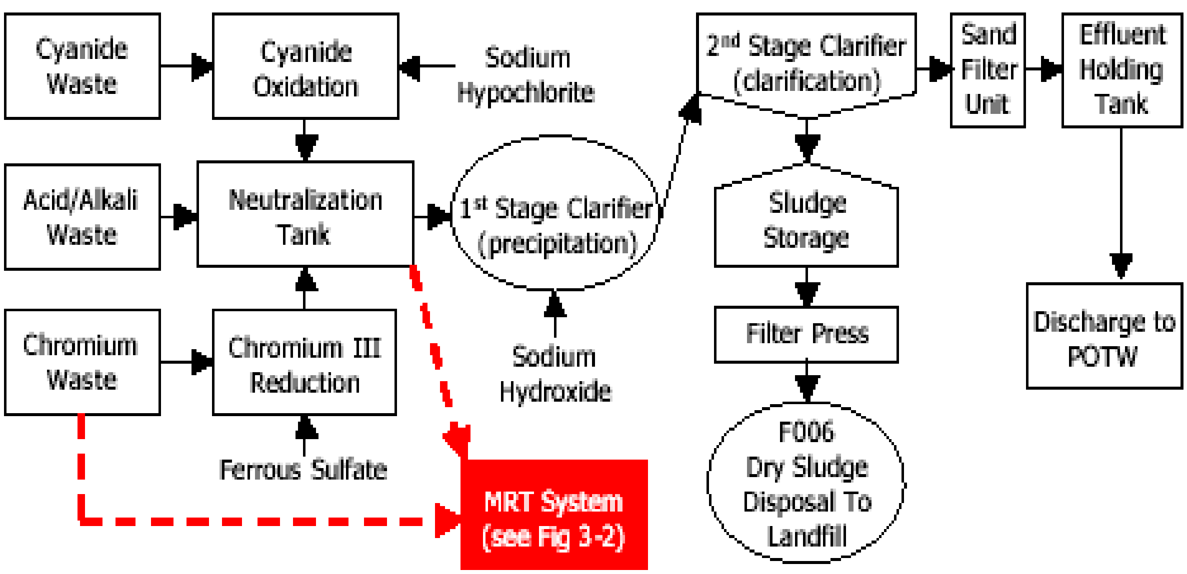

Figure 4. PSNS IWPF Treatment Processing and Location of MRT.

Table 4. PSNS Current and Proposed IWPF Effluent Standards.
(Volume > 1 million gallons discharge/year.)

Metal	Daily Maximum Concentration (mg/l)		Maximum Monthly Average (mg/l)*	
	Existing	Proposed	Existing	Proposed
Cadmium	0.17	0.02	0.17	0.01
Chromium	2.77	0.17	1.7	0.07
Copper	3.38	0.44	2.07	0.16
Manganese	none	0.04	none	0.03
Molybdenum	none	0.29	none	0.18
Lead	0.69	0.79	0.43	0.49
Nickel	3.20	1.90	2.38	0.75
Silver	0.43	0.05	0.24	0.03
Sulfide (as S)	none	31	none	13
Tin	none	0.03	none	0.03
Zinc	2.61	0.08	1.48	0.06

3.4 MRT PHYSICAL SET-UP AND OPERATION AT PSNS

The MRT system was installed in the PSNS Industrial Wastewater Pretreatment Facility as shown in Figure 4. The demonstration was "off-line" and performed in batch mode such that current IWPF treatment processing was not disrupted. Figure 5 shows graphically the design of the combined MRT chromium and acid/alkali system at PSNS. However, for the demonstration only columns 3 and 4 were used for operational testing. Columns 1 and 2 were for later scale up to full size MRT acid/alkali system. The smaller columns 3 &4 were used for testing of both Cr (VI) ions and acid/ alkali testing. The MRT system was demonstrated with a 15 ft x 15 ft x 10 ft skid mounted system. Each column was filled with 17.4 liters of expanded Superlig®. An optimum depth of bed was one with a 2 to 1 aspect ratio. The demonstration parameters were 1500 gals/12 hrs with a flow rate of two gal/min with breakthrough estimated +/- 500 gallons. The column loading rate was 4.06 gal/ min/ft^2. The optimal regeneration flow rate was 0.5 gal/min. The loading flow rate allowed the selected metals to have a single breakthrough so that the trailing column could remain well below compliance levels.

Testing was performed during FY99-01 where one to two tests were run per week. An operational test run was defined as completely processing 5,000 gallons of the waste stream, elution of the column, washing the column, and regenerating the column. For the acid/alkali waste stream, operational test runs were processed with wastewater from PSNS's neutralization tank after cyanide oxidation and chromium (VI) reduction to chromium (III) were completed. The metal cations recovered were Cd, Cu, Ni, Pb, Zn, and Ag with mixed bed of Superlig® 327 and Cr (III) with Superlig® 310. For the anion chromium (VI) a series of operational test runs were performed with chromium (VI) Superlig® 307.

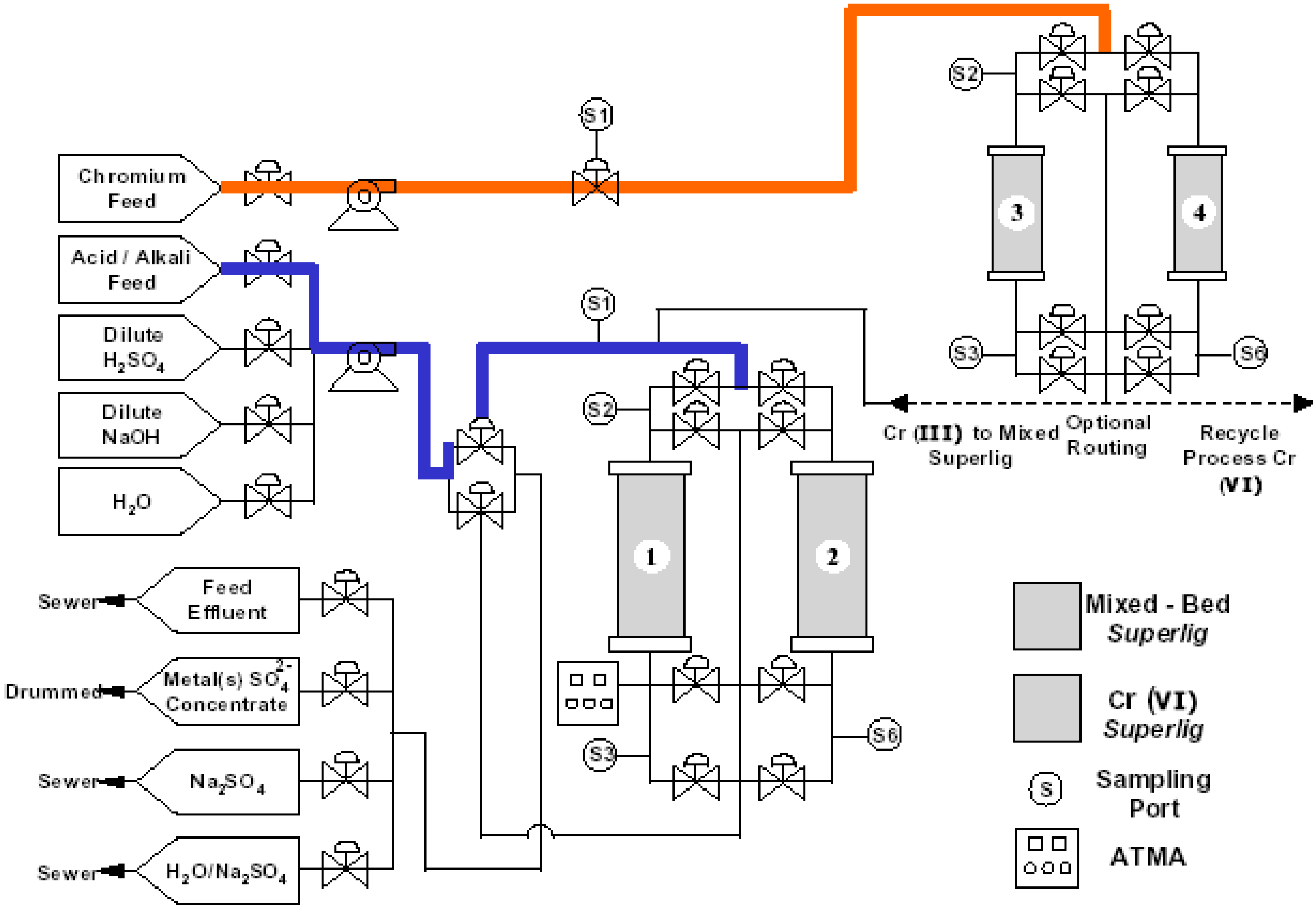

Figure 5. MRT System with Sampling Ports for Treating Acid/Alkali and Chromium Waste Streams.

3.5 SAMPLING/MONITORING PROCEDURES

Data collection followed the general guidance in PSNS's NAVSHIPYDPUGETINST P5090.26a. This analytical sampling plan was coordinated with PSNS Code 134, NFESC, and IBC Advanced Technologies. The sampling plan matrix for the waste streams was designed to determine: 1) efficiency in recovery of metals using MRT system compared to other absorbent metal ion technologies and 2) efficiency of MRT Superlig® columns.

1. To determine if the MRT met current compliance limits for discharge and future limits under the anticipated MP&M proposed Pretreatment Standards, samples were analyzed at locations shown in Table 5. The actual sampling locations are shown in Figure 5.

2. To determine the efficiency across the MRT column, samples were taken at ports shown in Table 5. Column capacity was obtained by determining loading rates (gram metal per kg Superlig® material). Lead column breakthrough was determined using the automated trace metal analyzer (ATMA) when the first Cu 2+ ions were at ppb levels (ref. 10). Full breakthrough was defined, as the point when the concentration in the influent is equals the concentration in the effluent, that is, the column has reached equilibrium. The efficiency of the regeneration was measured in bed volumes, and in the number of bed volumes to strip the columns with sulfuric acid to regenerate the Superlig® column. A bed volume (BV) for column 3 & 4 was 5.8 gals.

Table 5. MRT Sampling Port Parameters for Acid/Alkali Columns.
(See Figure 5 for sampling locations.)

Parameter	Column 1	Column 2
Discharge Limits	S1, S2 & S3	S6
Column Capacity	S3 & S6	S3 & S6
Column Breakthrough*	S3	S6
Regeneration Bed Volumes	S2 & S3	S3 & S6

* Determined by ATMA

3.6 ANALYTICAL PROCEDURES

3.6.1 Field Analytical Equipment

An automated trace metal analyzer (ATMA) was used to determine the breakthrough of copper during the test runs of the MRT. The ATMA, which was developed under a separate ESTCP program (Project #PP-199606) by SPAWAR (ref. 10), utilizes potentiometric stripping analysis (PSA). The automated trace metal analyzer was used as a diagnostic tool in determining if the engineering design of the MRT column was correctly configured. Field analytical equipment included, but not limited to, a HACH DR/2000 spectrometer, and pH and conductivity meters. Metal strip test kits were used during the operational running of the MRT system.

3.6.2 Selection of Analytical Laboratory

The PSNS Analytical Laboratory was selected to perform the analysis for the project. The analytical laboratory is accredited by the State of Washington Department of Ecology, #F001.

3.6.3 Selection of Analytical Method

The primary analytical method used by PSNS Analytical Laboratory is Method 200.7 Inductively Coupled Plasma (ICP) from the 200 Series under the Clean Water Act. This method is documented in "Methods for Chemical Analysis of Water and Waste, EPA-600014-79-020, revised March 1983. The updated version for this project is found in the Federal Register, Title 40 - Part 136 - 136 - Appendix C to Part 136, August 15, 1990.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

Operational tests were performed at various flow and regeneration rates, metal concentrations, and with contaminants such as surfactants and chelating agents. The results may be found in the ESTCP Technical Report (ref. 11).

4.1.1 Acid/Alkali Operational Testing

For the acid/alkali waste stream, the columns were loaded with Superlig® 327 for removal of Cd, Pb, Zn, Cu, Ag, and Ni. At PSNS, the analytical tests of the chromium waste stream showed 90% Cr (VI) and 10% Cr (III). In the MRT system shown in Figure 5, chromium (III) will be removed by using Superlig® 310 mixed with the Superlig® 327 in the columns. Operation test run #4 is presented in this report. The optimum flow rate 2 gals/min for influent feed and regeneration rate of 0.5 gals/min. The metals influent concentration is shown on Table 6. The data plots for test #4 are shown in figures on the next several pages. The analytical results show that magnesium (an alkaline earth metal) passed through the MRT column, that is, the % extraction was very low. The mass balance (mmoles effluent + mmoles eluent / mmoles influent) showed that magnesium was not retained on the MRT columns. This effect is expected as the 0.02 affinity constant (Log K) for magnesium is very low (see Table 1). For all heavy metals in test run #4, the metal concentration in the effluent stream was two orders of magnitude below PSNS monthly regulatory discharge limits. For lead (Pb), the % extraction was very high, but the mass balance showed that Pb was retained on the MRT column when eluted with 4 M sulfuric acid. Further testing showed that this was an analytical anomaly due to the low concentration of Pb. See the Technical Report for operation tests with higher concentration of lead (ref. 11). Further operational test runs of the acid/alkali waste stream showed that benign metals, Ca, Na, Mg, and K, passed through the MRT columns as predicted in Section 2.1. In Figure 6, breakthrough data are shown for the leading column at 500 gallons. The polishing column did not show breakthrough at 1500 gallons. Once breakthrough was established in the leading column, it was taken off line for regeneration. Figure 8 shows that the column was regenerated with a clean elution curve within two bed volumes.

4.1.2 Operational Testing for Cr (VI)

The operational testing for chromium (VI) showed that the chromium (VI) ion was preferentially extracted by the Cr (VI) Superlig® 307 columns for test run #23. See Figure 7. Equilibrium was established in leading column at 1600 gallons. When columns were eluted with 1 M NaOH, the Cr (VI) ion is maximized in first two bed volumes as shown in Figure 9. If it is desired to have chromium converted to the trivalent form, Cr (III), then columns are eluted with 4 M sulfuric acid (ref. 11).

Table 6. MRT Acid/Alkali Waste Stream Performance Data (Test Run #4).

Metal	PSNS Monthly Discharge Limits	MRT Influent (mg/l)	MRT Effluent (mg/l)	Extraction (%)	Mass Balance
Mg	NA	18.1	17.6	2.5	98
Cd	0.11	0.7	0.005	99.4	71.2
Cr Total	1.7	6.5	0.068	98.9	73.5
Cu	2.07	16.4	0.01	99.9	103.4
Ni	2.38	4.8	0.002	99.8	91.1
Pb	0.43	0.7	0.099	98.9	26.9
Zn	1.48	9.4	0.099	98.9	91.1
Ag	0.24	ND	NA	NA	NA

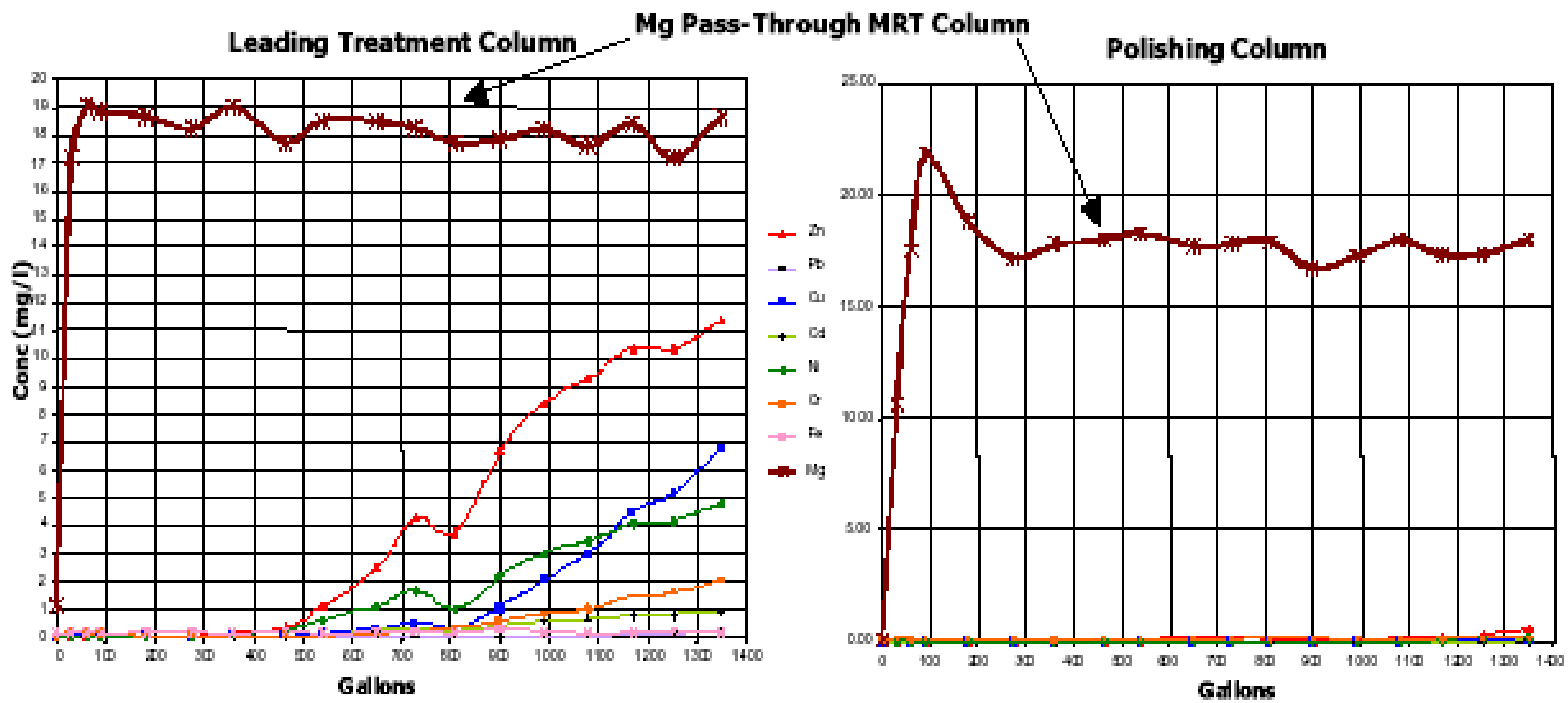

Figure 6. Acid/Alkali Performance Plot of Lead/Trail Column for Operational Test Run #4.

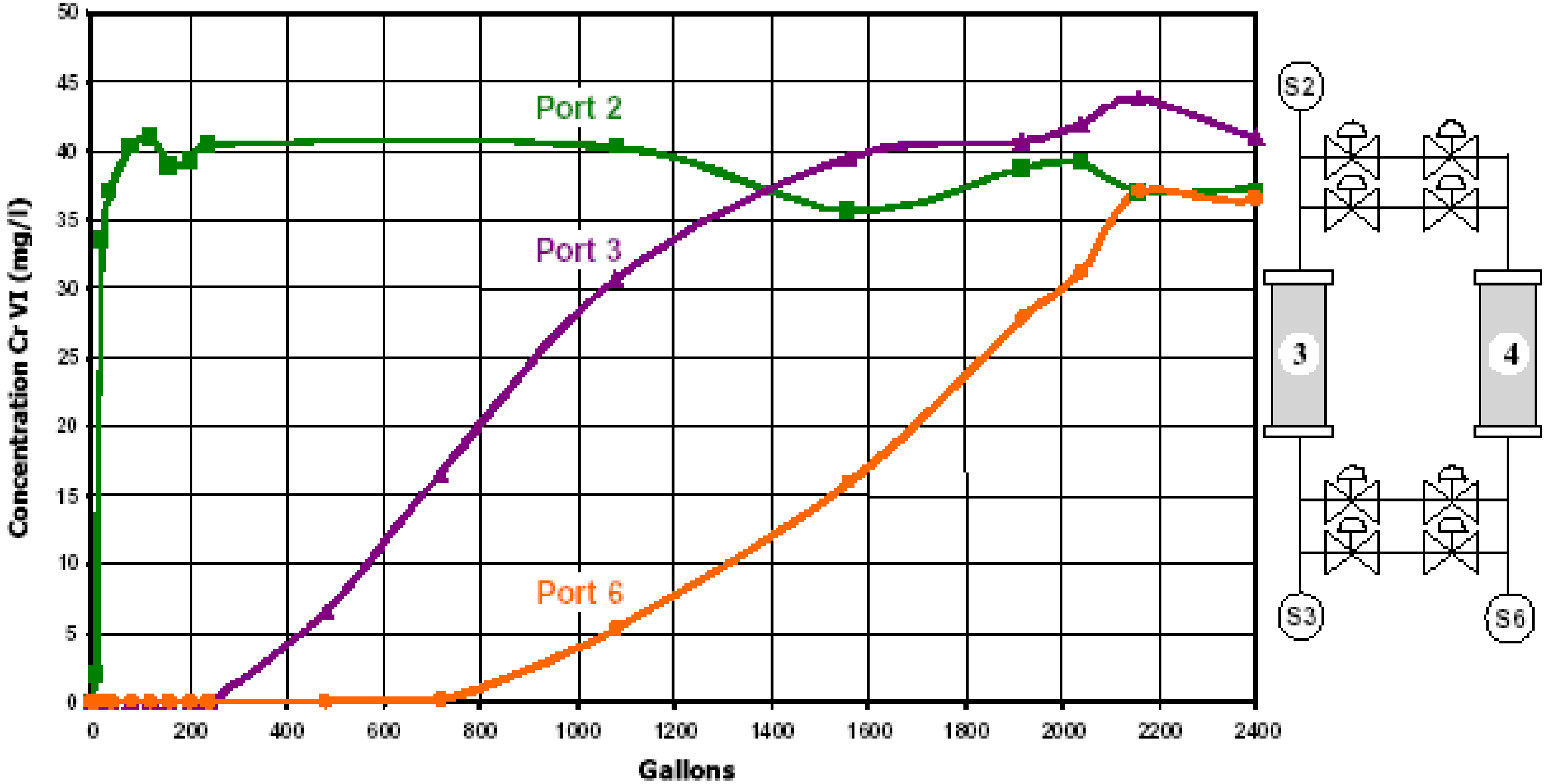

Figure 7. Chromium (VI) Performance Plot.

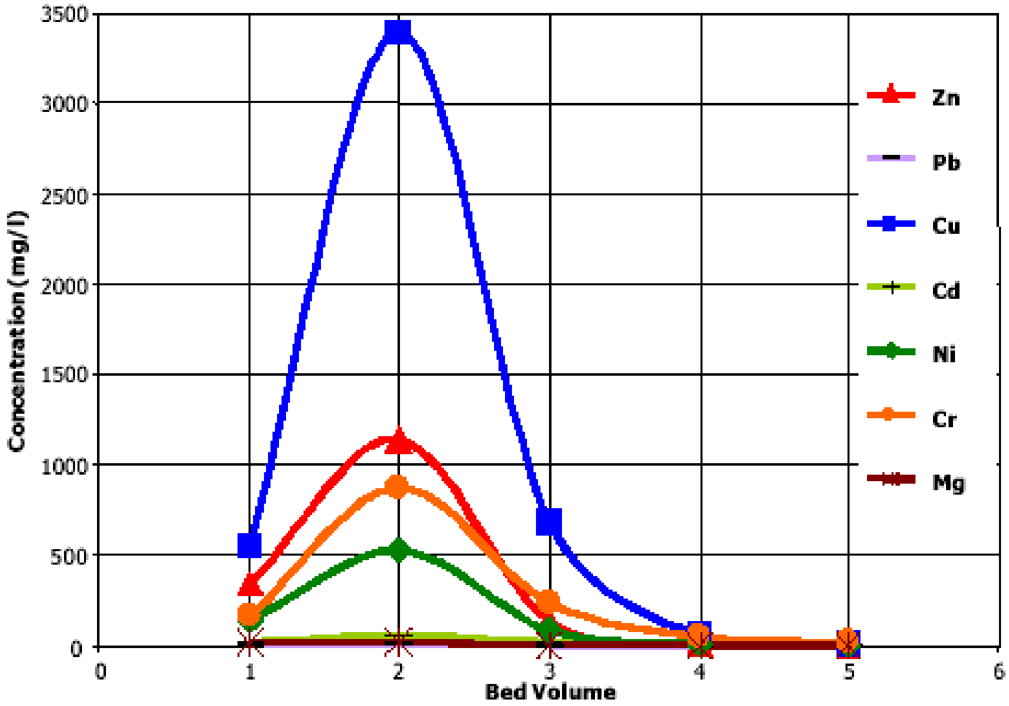

Figure 8. Acid/Alkali Regeneration Plot for Operational Test Run #4.

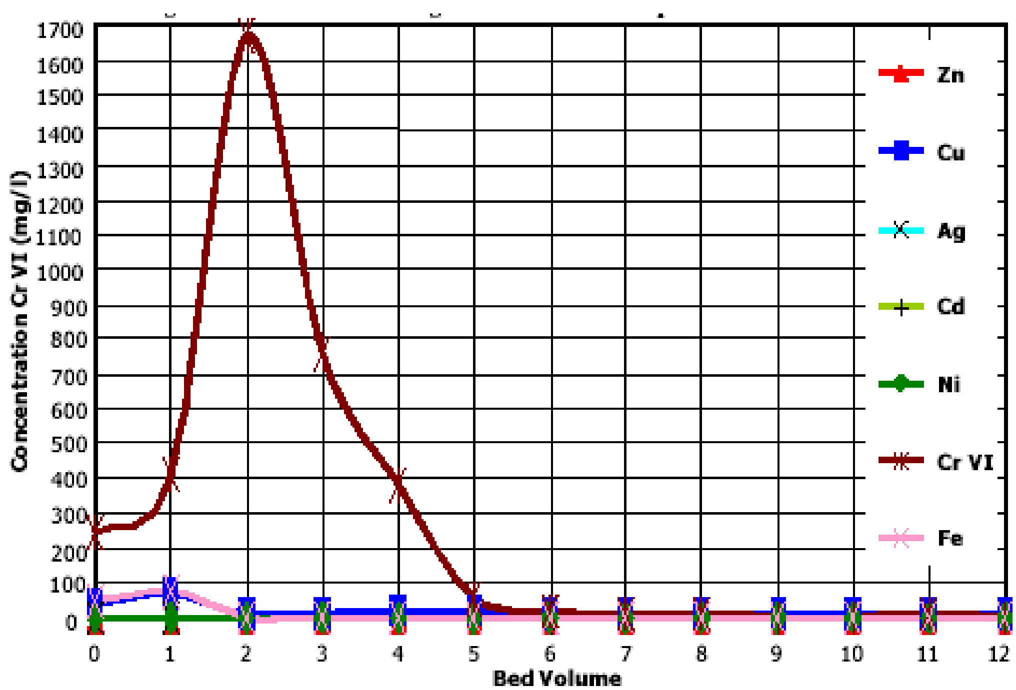

Figure 9. MRT 1M NaOH Regeneration for Chromium (VI) Recycle to Process.

4.2 PERFORMANCE CRITERIA

MRT expected performance and PSNS demonstrated actual findings are shown in Table 7.

Table 7. Expected Performance of MRT and Performance Confirmation Methods.

Performance Criteria	Expected Performance (Pre-Demo)	Performance Confirmation Method	Actual (Post-Demo)
Primary Performance Criteria - Qualitative			
Ease of Use	Minimal Operator Training	PSNS IWTP Operator Assistance	Found Technical Skill Required More Than High School Level
Primary Performance Criteria - Quantitative			
Meet CWA Reauthorization	99% Compliance of Expected Limits	Equilibrium Test Lab Analysis	Extract 98.8% of Heavy Metal Ions
Reduction of Sludge to Landfill	95% Metal Recycle Capability	Low Volume Metal Concentrate	90% Metal Recycle Capability
Cost of Conventional IWTP Replacement	1 Million/Year A.D. Little Analysis	ECAM Analysis	$1.26 Million/Year
Cost for Specific (Cu) Metal Ion Removal	$63K/Year IBC Advanced Technologies	Mining Industry Initial Results	$10K/Year <2.5 years payback
Heavy Metal Ion Reduction	99% Compliance of Expected Limits	EPA Method 200.7	Table 4 and Table 6
Factors Affecting Performance	Flow Rate & Column Bed Ratio 2:1 Aspect	Equilibrium Test Lab Analysis	Metal Ion Stripping 2:1 Aspect Required
Secondary Performance Criteria - Qualitative			
Reliability	High for Batch Ops Design Scaled to Range of Metal Ion Concentration	Experience from Demo Operation	Excellent Removal in Range of Metal Ion Concentration
Safety - Hazards - Protective Clothing	- Preparation of Acid Based Solutions - Pre/Post Operation Level B PPE	Experience from Demo Operation	- Preparation of Acid Based Solutions - Pre/Post Operation Level B PPE
Versatility - Intermittent Ops - Remote Monitoring - Other Applications	- Batch Operations - ATMA - Specific Metal Ion Recovery/Removal	Experience from Demo Operation	- Batch Operations - ATMA - Fluid Media: Radioactive, Domestic Waste, Seawater Mining
Maintenance - Required - Other Applications	- Filter Change - Multiple Chemical Additions	Experience from Demo Operation	- Filter Change - Multiple Chemical Additions
Scale-Up Constraints - Engineering - Absorption Rate - Regeneration Rate - Contamination %	- See Table 15 - 6 gal/min - 2.5 gal/min - Less than IX	Experience from Demo Operation	- Scaled for Demo - 6 gal/min - 0.5 - 1 gal/min - ½ CWA Limits

A.D. Little IWTP Economic Analysis (ref. 10)

4.3 DATA ASSESSMENT

Data required for comparative costing with other adsorptive technologies will be based on efficiency of 1) metal removal from the waste stream and 2) the MRT column capacity.

4.3.1 Efficiency of MRT System to Reach Lower Discharge Limits

The metal removal efficiency of the MRT to meet discharge limits is based on the extraction capability from the neutralization tank to effluent holding tank as shown on Figure 4. Table 6 shows that the leading column extracted all metals. The polishing column was maintained well below regulatory discharge level even after breakthrough of the lead column.

4.3.2 Efficiency Based on MRT Column Capacity vs. Ion Exchange

The second efficiency is across the Superlig® column itself. It is easy to vary the recycle time, but not the adsorption capacity of the Superlig® column. As stated in Section 2.1, in MRT the benign cations would pass through the column thus increasing the number of sites for the contaminant metals.

Table 8 shows that the amount of ion exchange resin required is double that of MRT Superlig® for the same size column. The number of available sites on an ion exchange column is less due to Mg taking up sites as well as heavy metal cations (i.e., 2654+3794 = 6448 number of sites taken on Ion Exchange column).

Table 8. Comparison of Superlig® Sites vs. Typical Ion Exchange.

Heavy Metals	Metals (mmoles) in Processed Wastewater
Cd	33
Cr	637
Cu	1,321
Ni	416
Pb	16
Zn	231
	Total: 2,654 mmoles
Earth Metals	
Mg	3,794
Ca	--
Na	--
K	--
	Total: 3,794 mmoles

Parameter Measured	Bench Scale	Actual PSNS
Mixed Bed Superlig® Capacity (mmoles/gram)	1.71	0.8
Typical Ion Exchange (mmoles/gram)	1.0	--
Grams of Superlig® Required	1,553	3,317
Grams of Ions Exchange Required	6,448	--

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5.0 COST ASSESSMENT

5.1 COST REPORTING

The Environmental Cost Analysis Methodology (ECAM) (ref. 13) was utilized to assess the cost of the MRT pilot demonstration at PSNS and to calculate the incremental profitability of the MRT technology relative to the conventional IWTP precipitation processes (called the Base Process). Costs for the PSNS demonstration are shown in Table 9. The costs in gray were for the demonstration only.

Table 10 shows the comparative capital and operating costs for the Base Process and the MRT Process for full-scale (30,000 gallons/24 hours) systems. Costs were estimated by PSNS personnel or from earlier IWPF studies at PSNS (ref. 5, 15). In Table 10, the cost estimate of $67,000 used for annual waste management, mainly sludges, is an average of over 14 DoD facilities (ref. 6). This is because, during the demonstration period at PSNS, a MILCON was underway at the Metal Finishing Facility and therefore a lower than typical volume of wastewaters was being processed at the IWPF, which resulted in a less than typical amount of metal hydroxide sludge being generated. There is no cost escalation of this waste management figure included in the ECAM for increasing landfill disposal costs. There are no labor savings while using MRT two operators are required to be present for safety reasons in the PSNS IWPF regardless of the work effort. Other non-variable cost factors not included in Table 10 are items such as document maintenance, worker compensation, health exams, compliance audits and manifesting.

Also, for the pilot demonstration at PSNS, costs for additional chemicals to treat wastewater when they occasionally become non-amenable to precipitation were not evaluated. However, the costs incurred for non-amenable copper-chelated wastewater for NAS North Island IWTP, and the potential savings using the MRT technology, are illustrated in Table 11.

5.1.1 MRT Cost Superlig® and Associated Equipment

The size of the pilot demonstration columns at PSNS was 17.14 liters each as shown in Figure 5 for columns 3 and 4. The mixed, polyacrylate-based Superlig® 327 and Superlig® 310 material cost $1800/kilogram (in 1999) for the quantities used in the pilot plant demonstration. For larger size MRT systems, the unit cost for the Superlig® would be less due to economies of scale in production. In addition, the bulk density of the support system for Superlig® material varies, i.e., for silica-supported Superlig® it is 0.45 kilograms/liter and for polyacrylate-supported is 0.21 kilograms/liter. For the pilot demonstration, the cost calculated was $12,958 (2 columns x 17.14 liters x 0.21 kilograms/liter conversion factor x $1800/kilogram).

In order to scale up to a full-size MRT system for PSNS, the volume of columns (1 & 2) would be 173 liters each. The cost for the Superlig® 327 and 310 would be $130,788 (2 x columns x 173 liters x 0.21 kilograms/liter x $1800/kilogram). The cost for the chromium (VI) Superlig® 307 is $111K for columns 3 & 4. (Note that the cost for the Cr (VI) Superlig® 307 is significantly lower in cost than at the time of the PSNS pilot demonstration.)

Table 9. MRT Demonstration Costs at PSNS for Acid/Alkali & Chromium Waste Streams.

Direct Environmental Activity				Indirect Environmental Activity Costs		Other Costs	
Start-Up		Operation & Maintenance					
Activity	Cost	Activity	Cost	Activity	Cost	Activity	Cost
Facility preparation and demobilization	$50K	Labor to operate equipment	$75K	Compliance audits (QA/QC)	$5K	Overhead assoc. with process	NA
Equipment design	$15K	Labor to manage hazardous waste		Document maintenance		Productivity/ cycle time	NA
Equipment purchase (Hardware/Skid)	$33K	Utilities	NA	Envr. Mgmt. Plan development & maintenance		Worker injury claims & health costs	NA
Installation	$10K	Mgmt/treatment of by-products	$10	Reporting requirements			
Training of operators	$9K	Hazardous waste disposal fees	$5K	Test/analyze waste streams	$25K		
Rental tanks	$3K	Raw materials		Medical exams (includes loss of productive labor)	NA		
Modification to Skid	$45K	Process chemicals	$20	OSHA/EHS Training			
Superlig® Material	$74K	Consumables and supplies	$15K				
Shipping Skid	$10K	Equipment maintenance	$10K				
		Training of operators	$3K				

Table 10. Cost Assessment Summary—Base Process and MRT Technology. (Capacity of 30,000 gallons/24 hours and Historical Range of Metal Concentration from Table 15.)

ECAM Cost Description	Base IWTP Process	MRT Process
Initial Investment Costs		
Miscellaneous Tanks	$234,000	$234,000
Final Effluent Tank	$68,000	$68,000
Cyanide Oxidation Unit	$146,250	$146,250
Chromium Reduction Unit	$105,300	
Chromium (Cr VI) MRT System		$144,000
Neutralization/Precipitation Unit	$98,280	
pH Control System	$15,000	$15,000
Flocculation/Clarification Unit	$108,810	
Acid/Alkali and Cr (III) Mixed Bed MRT System		$340,000
Sludge Storage Tank	$15,210	
Filter Cake/Brine Storage		$5,000
Belt Filter Press	$117,000	
Pre-Treatment Debris Removal		$20,000
Post-Treatment Sand Filters	$30,000	
Installation (30% Equipment Cost)	$281,355	$291,675
Total Capital Costs	**$1,219,205**	**$1,263,925**
Annual Operating Costs		
Direct Materials	$8,850	$8,030
Utilities	$55,650	$55,650
Direct Labor	$163,390	$163,390
Waste Management**	$67,000	$1,600
Regulatory Compliance	$27,500	$27,500
Revenues (By-Products)	$0	($6,800)
Total Annual Operating Costs	**$322,390**	**$249,370**
Net Present Value	**-$4,001,118**	**-$3,415,745**
Annual Cost Savings of MRT Process		
Discount Rate 2.7%, Lifetime 10 yrs, Payback 9 years		

** Personal Communication from Tinker Air Force Base for DoD statistics average over 14 DoD Industrial Wastewater Treatment Plants (ref. 5). Other data is from (refs. 4, 11, 12, 13 & 14).

5.2 COST ANALYSIS

In Table 10, the Net Present Value (NPV) of the Base Process was estimated to be -$4,001,118 and for the MRT Process was -$3,415,745, which indicates a small cost advantage for the MRT Process as demonstrated at PSNS. If MRT were being considered as a replacement for the conventional IWTP precipitation process, the payback would be period would be 9 years. However, if the MRT was installed as part of a MILCON project, the MRT system would offer certain benefits. The Net Present Value (NPV) of the Base Process was estimated to be -$4,001,118 and for the MRT Process was -$3,415,745, which indicates a small cost advantage for the MRT Process. If MRT were being considered as a replacement for conventional IWTP precipitation process, the payback period would be 9 years. However, installation of the MRT system would offer additional benefits. The MRT technology does not require as large a floor space as neutralization/precipitation and flocculation/ clarification units. Due to the smaller footprint (10' x 10' x 15') of the MRT system, cost savings may be realized in lower infrastructure, which is not accounted for in ECAM. The MRT technology is also able to achieve lower discharge limits than the conventional process, which would avoid the occasional requirement with the conventional process to manifest batches off-site to a hazardous waste contractor.

Although the MRT pilot demonstration at PSNS showed only a small cost advantage as compared to conventional technology, four alternative scenarios for MRT application are described below, and associated equipment costs are summarized in Table 12. Due to the many configurations that MRT can assume, a DoD activity must choose the scenario that best meets its compliance/pollution prevention needs for heavy metal recovery/recycle.

Scenario (1) and Scenario (2) were demonstrated at PSNS and cost estimates are in Table 10. For the other four scenarios, the ECAM analysis was not performed but the source of data and method of estimation is referenced.

1) <u>Mixed Bed Acid/Alkali With Chromium (III)</u>: The cost of a full-scale mixed bed for acid/ alkali with chromium (III) would be $340,000 assuming that the Superlig® 327 and 310 are not discounted for larger quantity purchase. In addition, the actual cost of the MRT would depend on many factors including the utilities available, degree of automation desired, and local site requirements (ref. 13).

2) <u>Single Metal Add-on Mixed Bed Chromium (VI)</u>: A chromium (VI) MRT lead-trail column system, as shown in Figure 5 for PSNS, is estimated to cost $144K, assuming that the major pumps, valves, flow meters, etc are already installed on the skid for acid/alkali with chromium (III) mixed bed MRT as described in (1) above (ref 13).

3) <u>Pretreatment (Chelated Copper)</u>: At the NAS North Island IWPF, the influent from certain maintenance operations chelates the copper, which then cannot be treated by the conventional precipitation process (ref. 16). Feasibility testing has shown that processing this chelated-copper waste stream through a MRT column containing copper Superlig® 311 would break the copper-chelated bond (ref 12). The conventional precipitation process could then subsequently treat the wastestream because the copper would be present as the free, unchelated copper $^{2+}$ ion.

The capital cost for a mono-metal copper recovery MRT system was estimated as $85,000. In this scenario, the MRT is an add-on batch processing system used for 5,000 gallons/month of chelated copper wastestream. The savings in labor and disposal cost would provide a payback of less than 2 years. The labor for the base process is high due to the time it takes operators to perform analytical testing and manifest the chelated copper wastestream.

Table 11. MRT Payback for Chelated Copper Treatment.

Category	Base Process ($K/Yr)	MRT Process ($K/Yr)
Capital Cost	0.0	85
Labor	41.0	8.0
Materials	2.7	2.0
Disposal	20.0	0.0
Total	63.7	10.0
Cost/Gallon	$1.06	$0.17

Net Savings: $0.895/gal x 60,000 gal/yr = $53,700/yr
Payback: < 2 years

4) Point Source for Total Chromium: A chromium (VI) and (III) MRT could be installed in a Metal Finishing Facility (MFF) such as at PSNS. Both Cr (VI) and Cr (III) Superlig® columns are required because the discharge limit is for total chromium. If MRT is installed as an alternative technology during a MILCON, greater savings can be realized than as an add-on to the base process (ref 11). However, by recycling pure chromium wastestreams, significant savings could be realized as chromium and nickel wastestreams are valued for stainless steel production (ref. 10, 13). See Section 6.1.2.

5) Sequential/Selective for All Target Metals: Sequential selective recovery for mono metals concentrated streams was bench tested using acid/alkali and chromium wastewaters from NADEP North Island (ref. 12). Figure 10 shows the sequential selective recovery of metals, which generated five pure metal streams for recycle. The number of columns would be 8 columns (4 lead and 4 trail). The cost estimate as an alternative technology would only be cost effective if the activity was directly recycling these pure metals streams. See Section 6.1.2 for recycle strategies.

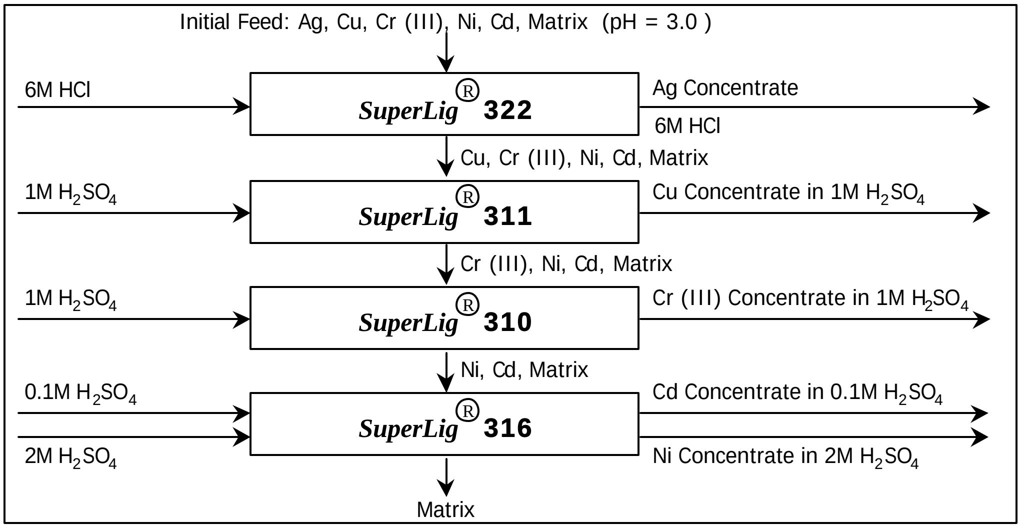

Figure 10. Sequential Selective Recovery Metals NADEP North Island Acid/Alkali Stream.

6) Membrane Embedded Superlig® Polishing: MRT could be used to polish metals in high volume waste streams to very low levels (5ppm to 1ppb) for new regulatory requirements. It has been determined that a membrane embedded Superlig® system would be more cost effective for polishing than the packed bed column that was demonstrated at PSNS. Reference 9 gives more details on embedded Superlig® materials. IBC Advanced Technologies, Inc, estimated the cost of a membrane embedded Superlig® polishing system for > 1 million gallons but < 2 million gallons per year, to be $86K without automation (ref. 9, 12).

Table 12 shows the comparative cost estimates for the above six scenarios based on bench scale studies, feasibility studies, and PSNS pilot demonstration.

Table 12. MRT Equipment Cost Estimates ($K) for Various Scenarios.

MRT System	Place	Acid/Alkali Superlig®	Skid	Cr VI Superlig®	Skid	Cr III	Skid	Cu Superlig®	Skid	Total Cost
1. Mixed Bed* Acid/Alkali with Cr (III)	PSNS	$105	$209			$6	$20			$340
2. Single Column* Cr (VI) Addition to Mixed Bed	PSNS			$111	$33					$144
3. Pre-treatment Chelated Cu	NAS NI							$52	$33	$85
4. Point Source Plating Shop Total Cr Columns	PSNS			$111	$50	$26	$35			$222
5. Sequential* Selective Columns	NADEP NI	$228	$242			$26	$36			$532
6. Membrane Embedded Superlig® Polishing System 10 Year	PSNS	$25	$30	$5	$10	$6	$10			$86

5.3 COST COMPARISON

Ion exchange is probably the closest technology for comparison with MRT. In 1995, A.D. Little (ref. 5) investigated 1) ion exchange/electrolysis and 2) ion exchange/electrodialysis as potential chromium recovery/recycle systems. For the first system, ion exchange/electrolysis used both cationic and anionic columns for the Cr (VI) and Cr (III) ions, respectively, with electrolysis to recover the chromium ions. The capital costs for a 30 gal/min ion exchange/electrolysis system was $259,740. The process is commercially available, but its use on DoD facilities has not been documented. For the second system, ion exchange/electrodialysis, the cost estimate with a flow rate of 30 gal/min was $251,000 (ref. 5). MRT cost estimates in Table 12 compare favorably with these two ion exchange systems. The advantage of MRT is a lower infrastructure, i.e., one component rather than several in-line processing units. In addition, MRT can reach lower metal concentration levels than ion exchange as described in section 2.1.

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6.0 TECHNOLOGY IMPLEMENTATION

6.1 COST OBSERVATIONS

The revenues for selling the metal laden concentrate were estimated to be $6,800 in Table 10. This latter assumption is being verified by a study in progress at PSNS as discussed in Section 6.1.2 concerning the best strategy for "fine tuning" the metal laden waste streams for selling to metal recycle vendors (ref. 17). MRT, if not used as an industrial wastewater treatment system, can be used to separate valuable mono-metal concentrates. In order to consider the use of MRT, as an alternative technology for industrial wastewater treatment, the following factors need to be analyzed: a) regulatory changes and b) the capability of the alternative technology to make the F006 waste more amenable to recycling.

6.1.1 Regulatory Issues

If the MP&M rule is changed as anticipated to lower discharge limits (see Table 4), conventional precipitation treatment will require pH to be close to the maximum range for each metal in order achieve these lower discharge limits. For example, cadmium will require a high pH of 11. The additional costs of O&M of the conventional precipitation system due to rebatching to meet compliance limits may increase the attractiveness of installing an MRT system. Secondly, landfill disposal costs are increasing due to the loss of capacity, impact of "land ban" restrictions, and increased disposal taxes. From 1980 to 1990, disposal fees increased by 160% and the Superfund Waste Tax was increased by 27%. The liability factor adds consideration of potential future cleanup sites that would be incurred if a disposal site became a Superfund site. Because what hazardous waste recycle vendors accept is treated on site, presumably the liability factor for this option would be considerably lower than land disposal option (ref. 18).

6.1.2 Strategies for Recycle of F006 Waste Using MRT

Due to this increasing cost to landfill, potential recycle scenarios need to be proposed. NFESC is currently researching the cost benefit of selling the IWPF's hazardous metal sludge or as a MRT concentrate to commercial recycle vendors (ref. 17). There are 10 or more established recycle companies in the U.S. that accept F006 waste as shown in Table 13. Table 14 shows the preferences for certain types of metal waste stream concentrates or sludges. For example, a metal waste stream with high chrome and nickel containing less than 2% copper is marketable. In addition, copper alone is a valued metal waste stream. Looking at the historical influent waste stream at PSNS in Table 15, that there is a high content of copper, chromium, and nickel. The waste stream does not contain tramp metals nor is the phosphorus content high. In order to recycle with a cost benefit at PSNS, an MRT system could be installed to take out the copper from the influent waste stream, allowing the remaining feed to be processed by the conventional precipitation method. The copper concentrate would be manifested separately to the recycle vendor. The sludge that remained from conventional processing could be recycled to a vendor accepting metal sludge for the stainless steel manufacturing industry, i.e., high in nickel and chromium metals.

Table 13. U.S. Metal Reclaimers Processing > 1.1 Million Tons/Year.

Company	Years in Business	Waste Types	Metals Accepted	Process	Process Capacity Tons/Year	# Plating Shops Clients
Horsehead Resource Development Co.	1993	F006 F019	Zn, Pb, Cd, Fe	Rotary Kiln	27,000	100
Inmetco	1978	F006	Cr, Ni, Fe, Mo, Cu	Pyrometallurgical	56,000	150
RECONTEK		F006	Zn, Cu, Precious Metals	Hydrometallurigical	33,000	
CP Chemicals	1950	F006 D002&4 D007&8	Pickeling Solutions, Spent Plating Baths, Strippers	Hydrometallurigical	120,000	1,000
World Resources Company	1980			Hydrometallurigical Pyrometallurgical		800
Encycle/ Texas, Inc.	1988	F006	Cu, PB, Zn, Ni	Chemical/ Hydrometallurigical	25,000	150
Alpha Omega Recycling		F006	Cr, Cr-Ni mix, Cu	Acid Leaching/ Selective Precipitation	5,500	100
Cyano Corp. Michigan		F007 F008 F009	Cyanide Waste	Electrowinning	2,200	50

10-15 Metal Recyclers with ~1.1 million tons/yr 13,470 Plating Shops each generating 79 tons/yr for a total of 1,064,130 tons/yr

Table 14. Metal Vendor Marketability of Industrial F006 Waste from IWTPs.

Potential Recycle	Limited / Surcharge
• Nickel & Copper with Chromium <2.0%	• Chromium Only
• Chromium & Nickel with Copper <2.0%	• Phosphorous <0.05%
• Copper Only	• Moisture <35%
• Nickel Only >10%	• Tramp Metals (Arsenic and Mercury)
• Hydroxide (OH) Precipitated Sludges	• Sulfide Precipitated Sludges
• Flocculation Anionic Polymers	• Flocculation Alum and Ferric Compounds

Table 15. Analysis of PSNS Influent Waste Streams and Sludge Samples.

Metal	*Historical Ave Influent (mg/l)	MRT Run #1 (mg/l)	MRT Run #4 (mg/l)	MRT Run #20 (mg/l)	Treated Sludge #20 (mg/kg)
Zinc	23.0	30	9.8	224	18,800
Lead	1.30	0.52	0.61	6.28	759
Copper	31.0	29	16.08	263	27,600
Silver	0.44	0.07	0.027	1.15	184
Cadmium	2.61	1.07	0.772	19.1	1,510
Nickel	6.61	3.36	5.05	35.8	3,870
Chromium	60.0	16.1	8.23	65.8	12,600
Phosphorous	Unknown				3,800

*Walter Hunter supplied data collected from PSNS Industrial Wastewater Pre-Treatment Facility.

6.2 PERFORMANCE OBSERVATIONS

The main factor affecting performance of metal ion removal is kinetics (speed of flow versus amount of Superlig® present) for the packed bed column. Other configuration options have been suggested under Section 5.2. The temperature limitation of the MRT system is based on the polymeric bead support that has a 90-95° C limit. The efficiency of an up front oil/water separation system and filtration system will greatly enhance the long-term usage of the MRT columns.

6.3 SCALE-UP

This technology is currently available for off-the-shelf procurement. However, it must be customized for each site and the customer's specific requirements. The design of a MRT system for a particular site requires a treatability test for the particular wastewater stream. The MRT system pilot-scale demonstration at PSNS can be modified to a "full scale system" for the current PSNS acid/alkali waste stream entering the IWPF. The costs that will be incurred will be for larger pumps and additional Superlig® material for the columns. Prior feasibility tests to the ESTCP pilot demonstration have determined that the design parameters scale linearly with flow, cycle time, and regeneration requirements of the customer (ref. 12). Table 16 shows the design parameters for two MRT Systems based on the time requirements of 24-hrs per day versus business hours only processing. The amount of Superlig® in the column must be increased for the business hours only processing. MRT can handle increased flow rates by using membrane embedded Superlig®. However, PSNS choose to use the packed bed column configuration.

Table 16. MRT Design Parameters for Scale-Up.

System Parameter	Units	Quantity in 24 Hours	Business Hours Only
Feed Flow Total (per year)	gallons	1,638,600	1,638,600
Feed Flow Rate (average)	l/min.	11.88	49.9
Feed Flow Cycle	gallons	39,014	163,860
Feed Time Cycle	hours	204	204
Cycles Per Year	number	42	10
Superlig® Per Column	pounds	26	109
Eluent Flow Rate	l/min.	8.58	36
Eluent Cycle Time	min.	6.06	6.06
Total Cycle Time	hours	204	204

6.4 OTHER SIGNIFICANT OBSERVATIONS

The number of regenerative cycles could not be tested in the time span of the demonstration. Previous experience in the mining industry indicates a multi-cycle lifetime in the thousands.

6.5 LESSONS LEARNED

The initial research, development, testing and evaluation for MRT was to be able to recycle metal ions back to the industrial process. Studies were conducted that showed that the metals from the industrial waste stream could be sequentially and selectively removed as concentrated mono-metal streams (ref. 3). However, recycling to process may not be allowed due to strict military specifications at some DoD facilities. Secondly, if metals are recycled to process, say in a plating facility, the vendor's warranty of the plating bath may be invalid.

6.6 END-USER ISSUES

It is important that the end-user provide an accurate picture of the intent for the MRT application as discussed in Section 5.2 such as mixed bed, single mono-metal, or sequentially selective metal recovery. In addition the end-user must provide the following information at a minimum in order to correctly size a MRT system: 1) concentration range of influent waste stream to be treated; 2) pH of waste stream; 3) metals to be removed to what level (ppm) in the effluent, and 4) average flow rate for processing.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

Depending on the nature of the discharge under the CWA, DoD agencies will be required to meet the NPDES for direct discharge and the General and Categorical Pretreatment Standards for the indirect discharges. EPA is proposing effluent limitations guidelines and pretreatment standards for industrial wastewater discharges from metal products and machinery (MP&M) facilities. The metal products and machinery industry includes facilities that manufacture, rebuild or maintain metal products, parts and

machines. Since 90% of a typical IWTP volume of wastewaters is from metal finishing facilities, the impact in processing will require alternatives pretreatment technologies to replace existing system or provide final polishing of the effluent waste stream. In March 2000, a modification to 40 CFR Part 262 was made by EPA. Under this modification, the generators can extend their accumulation of F006 waste up to 270 days so that more attractive, larger quantities of metal laden waste may be sold to metal recycle vendors.

Every DoD IWTP must meet the Federal Categorical Pretreatment Standards for discharge under the CWA. However, the IWTP must also meet standards set by the local POTW if an activity is sewering the pretreated wastewaters. The POTW's standards are typically lower than the federal standards. As discussed in Section 6.1 there are various scenarios to accomplish regulatory compliance. If the MRT is used as a polishing unit, then this modification of the treatment system must be reported to regulators. If the MRT were to be used as a source recycling technology, say for the removal of Cr (VI) in the metal finishing facility, then there is no permitting issue.

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APPENDIX A

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